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Impact of Gasohol on Automobile Evaporative and Tailpipe Emissions

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16. ABSTRACT

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Two passenger cars, a 1977 Ford Mustang II and a 1979 Ford LTD II, were tested, emissions analyzed for hydrocarbons, ethanol, carbon monoxide, and nitrogen oxides content, and fuel economy and driveability examined. Both tailpipe and evaporative emissions were examined. The procedures used are described in the Federal Register for emissions certification.

Generally, the addition of ethanol to gasoline reduced tailpipe emissions of hydrocarbons and carbon monoxide, but increased oxides of nitrogen. Driveability problems were experienced with the LTD-II. The use of gasohol substantially increased evaporative emissions from both cars, but fuel economy impact was negligible.

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ABSTRACT

National interest is growing in the use of gasohol, a blend of ethanol and unleaded gasoline, as an alternate fuel to gasoline. In order to assess its viability as a transportation fuel, gasohol's impact on vehicle emissions, fuel economy, and driveability must be considered, along with the cost of production and the physical compatibility of ethanol with gasoline.

Both tailpipe and evaporative emissions were examined on two passenger cars, a 1977 Ford Mustang II and a 1979 Ford LTD II. In addition to determining total hydrocarbon, ethanol, carbon monoxide and nitrogen oxides content, fuel economy and driveability were also examined. The procedures used for emissions measurement are described in the Federal Register for LDV Certification.

Five fuels were used in the program, including two base fuels and three gasohol blends, each car tested with the fuels in sequential order. Generally, the addition of ethanol to gasoline reduced tailpipe emissions of hydrocarbons and carbon monoxide, but increased emissions of nitrogen oxides. Since the stoichiometric air/fuel (A/F) ratio for ethanol is lower than that for gasoline, adding ethanol to gasoline results in a lean shift in combustion stoichiometry, which generally results in a decrease of hydrocarbons and carbon monoxide emissions and an increase in oxides of nitrogen emissions. Coldstart driveability problems were experienced with the LTD II. Little change in fuel economy was observed with either vehicle. The use of gasohol substantially increased the evaporative emissions of both vehicles.

Two final areas examined during this program were the adequacy of a one hour test period for determination of hot soak evaporative emissions and the sensitivity of the emissions to vehicle preconditioning. Hot soak evaporative emissions increased during the second hour of examination and both tailpipe and evaporative emissions were sensitive to vehicle preconditioning.

INTRODUCTION

As U.S. petroleum demands continue to exceed domestic availability, there is a need to define an alternative to gasoline as a primary transportation fuel. Gasohol, ethanol blended with unleaded gasoline, offers an attractive alternative because of this country's capacity to grow grain crops suitable for ethanol production. The use of alcohol with gasoline is not a new idea. Almost since the basic gasoline internal combustion engine was invented, alcohol has been considered a potential fuel. The U.S. Department of Agriculture published in 1907 many

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of the advantages and limitations of alcohol that are still discussed today.(1)* Ethanol has become a primary transporation fuel in Brazil; it is also used with motor vehicles in other countries, but generally with special economic incentives to promote its use. In January 1980, the Carter Administration outlined a fuel program for the U.S. that offers tax credits and waivers, federal loans and loan guarantees to increase interest in producing ethanol for use in gasohol.

After a stability that lasted many years, gasoline prices have increased rapidly since 1974 to a national average pump price of over one dollar, with current consumption at about 7,000,000 barrels per calender day.(2) The rate of ethanol production is currently about 33,000 barrels per day, with 75% produced by hydration of ethylene derived from petroleum.(2) Most ethanol produced in this manner is consumed as an industrial chemical. The remaining 25% is produced in hundreds of small plants by fermentation of corn, wheat, or other agricultural crops. Essentially all of the ethanol made by fermentation is used in drugs, cosmetics, and beverages. In early 1979 the wholesale price of ethanol ranged from $1.20 to $1.40 per gallon.(2) Although gasohol has received special economic considerations (exemption from state taxes) to encourage its use, the fuel is still more expensive than the gasoline it replaces. Also, this price does not reflect the construction costs associated with new ethanol-producing plants necessary to meet future U.S. needs. At a fuel consumption rate of 7,000,000 barrels per calendar day, 700,000 barrels of ethanol would be needed to produce a gasohol blend of 10% ethanol in gasoline, which greatly exceeds current production rates. If gasoline costs exceed that of ethanol, gasohol might become an economically feasible alternative to gasoline. However, gasohol's impact on vehicle emissions, fuel economy, and driveability must be considered.

A brief study of the physical properties of ethanol can help to predict its impact on emissions when added to gasoline. Table I compares the physical properties of ethanol to octane, a hydrocarbon representative of gasoline.(3) The most noticeable difference between the two compounds is the oxygen content of ethanol and its effects on the stoichiometric air/fuel (A/F) ratio. Stoichiometric combustion occurs when chemically equivalent amounts of fuel and oxygen are present. Since the stoichiometric A/F ratio for ethanol is lower than that for gasoline, adding ethanol to gasoline can be equated to reducing the amount of fuel in the intake charge of the engine. This "leaning" of the intake charge can either decrease or increase exhaust emissions and fuel economy, depending on the base tune of the carburetor relative to stoichiometric combustion of gasoline. For vehicles operating with a base tune rich of stoichiometry, the addition of ethanol would cause a shift to leaner combustion resulting in decreased emissions of hydrocarbons and carbon monoxide and possibly improved fuel economy. For vehicles operating with a base tune lean of stoichiometry, driveability problems may appear. The leaning effect of gasohol becomes particularly important during cold-start operation. The normal low-temperature fuel enrichment needed for smooth engine operation may be inadequate with gasohol. Typical driveability problems, i.e. stalling, rough idle, and sluggish acceleration, could be encountered.

Figure 1 illustrates the relative range of exhaust emissions of total hydrocarbons (THC), carbon monoxide (CO), and oxides of nitrogen (NOx), as related to the A/F ratio.(4) As indicated, fuel economy or fuel consumption (FC) is also a function of the A/F ratio.(5) The lowest fuel consumption is generally realized slightly lean of stoichiometric combustion. Figure 1 illustrates that a lean shift in the A/F ratio generally results in a decrease of THC and CO emissions and an increase in NO_x emissions. If the base-line A/F ratio is lean of stoichiometric, a lean shift could reduce NO_x, although automobiles are not normally operated that lean.

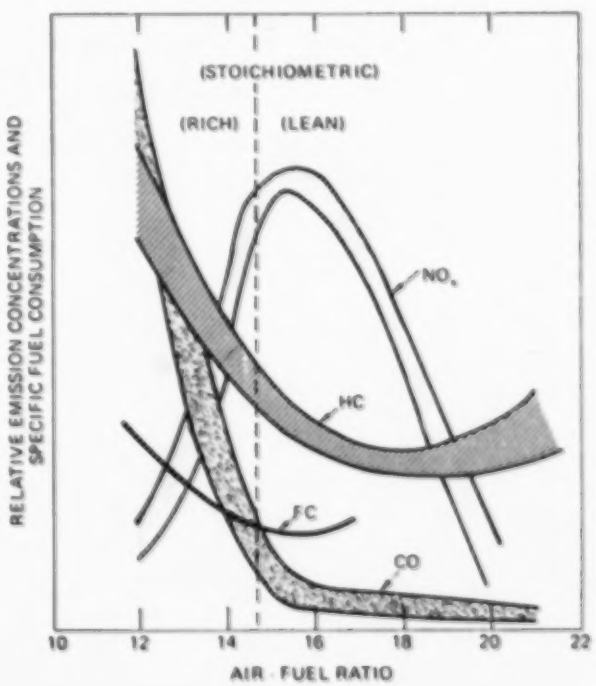

Fig. 1 - Effect of air-fuel ratio on exhaust emissions and fuel consumption

*Numbers in parentheses designate References at end of paper.

Returning to Table I, the low net heat of combustion, or energy content, of ethanol may also prove to be a disadvantage of adopting gasohol as a motor fuel. A decrease in fuel economy would be expected for gasohol compared to gasoline because of the lower energy content of ethanol. An additional item of interest is the comparison of ethanol energy content and energy consumption in the manufacturing process. It has been demonstrated that for every BTU of energy made available as ethanol, 1.4 BTU's of energy are consumed in production.(2) Perhaps more advanced production techniques or the use of solar energy during the manufacturing process will one day lessen the importance of this consideration.

The primary objective of this study was to examine the impact of gasohol on vehicle evaporative and tailpipe emissions. The results obtained are probably typical of vehicles with emission control equipment configured as with the primary test vehicles. However, other emissions control configurations may respond to the use of gasohol fuel in an entirely different manner.

EXPERIMENTAL

The two passenger cars used for testing were a 1977 Ford Mustang II and a 1979 Ford LTD II. The Mustang was selected as representative of vehicles with a first level of evaporative control. Fuel-tank emissions from this car were controlled with an adsorption/regeneration carbon canister, but carburetor emissions were essentially uncontrolled. The 1979 LTD II was selected as representative of vehicles with a more advanced series of evaporative control systems that control both carburetor and fuel tank emissions with separate canisters. Pertinent specifications for the selected test vehicles are given in Table II.

Each vehicle's gas tank was modified by insertion of a thermocouple plug to measure fuel temperature during the evaporative test sequence, and to facilitate removal of waste fuel. Each vehicle was also equipped with new charcoal canisters which were conditioned by running 5 urban driving cycles, and a new catalyst was installed and conditioned with 250 miles on the 1977 Mustang II prior to experimentation. The Mustang was operating with a rich base carburetor tune as indicated by a 1.7% CO concentration at idle versus a 0.50% certification value.

Table I - Properties of ethanol and octane.

Physical property	Ethanol	Octane
Chemical formula	C_2H_5OH	C_8H_{18}
Molecular weight	46	114
Oxygen (% by weight)	34.8	-
Stoichiometric A/F ratio	9.0	14.6
Net Heat of combustion (1×10^3 BTU/gal)	76	115
Latent heat of vaporization (1×10^3 BTU/gal)	2.6	0.8

The five fuels used in the program were:

1. indolene clear,
2. indolene (Fuel 1) with added ethanol,
3. summer-grade unleaded regular octane fuel,
4. Fuel 3 with added ethanol, and
5. blended gasohol with added ethanol and distillation characteristics similar to Fuel 3.

Table III contains detailed specifications for each of the commercially blended fuels, including Reid Vapor Pressure (RVP), distillation information, API Gravity, and the percentage content of paraffinic, olefinic, and aromatic hydrocarbons and ethanol. Fuel 1 and Fuel 2 were chosen to indicate changes in emissions when ethanol is blended with the certification fuel. Fuel 3 was selected as representative of an average summer grade fuel, while Fuel 4 represents a commercial blend of ethanol with Fuel 3. Fuel 5 was blended to match the distillation characteristics of Fuel 3. Although it is expected that Reid Vapor Pressure increases with the addition of ethanol, analyses of these fuels showed just the opposite. This suggests that some light ends (butane, etc.) may have been lost during the blending process. This conclusion is supported by the higher initial boiling point of the gasohol fuels. Also the presence of low levels of ethanol in the base fuels suggests poor blending practice.

Each car was tested with Fuels 1-5 in sequential order. To ensure adequate conditioning (fuel replacement) when the fuels were changed, the vehicles were driven on a standard road course, the Raleigh Road Route (RRR). The RRR is 44 miles long, involves 13 required stops and has an average speed of 45 mph. To ensure a standard canister purge period prior to each emissions test, each vehicle was parked for a minimum of 1 hour after the completion of the RRR, and then was driven on the dynamometer over an LA-4 cycle to condition the vehicle for the following day's evaporative test.(6)

The vehicle test sequence is presented in Figure 2.(7) One complete series includes a diurnal evaporative test, an urban dynamometer driving test, and a hot-soak evaporative test. The diurnal test typifies emissions released by the vehicle during normal night to midday ambient temperature increases by heating the fuel from 60°F to 84°F. Only the fuel tank "sees" the temperature increase in the simulation test.

Table II - Vehicle specifications.

Specification	Vehicle 1	Vehicle 2
Make	Mustang II	LTD II
Manufacturer	Ford	Ford
Engine Family	302 CID	351 CID
Emissions Control	EGR, CAT, PCV, single canister (fuel tank)	EGR, AIR, CAT, PCV, dual canister (carb. & fuel tank)
Mileage	10,000	400
Inertial weight (pounds)	3,000	4,500
Fuel tank capacity (gallons)	16	21

Table III - Test fuel specifications.

Specification	1	2	3	4	5
RVP	9.15	9.10	9.85	9.65	9.40
IBP, °F	91	101	89	95	94
10	138	129	124	121	124
50	238	212	231	213	242
90	322	320	361	356	362
EP	341	359	405	413	408
Ethanol (% vol)	1.4	6.2	0.86	8.1	10.1
API gravity	59.8	58.7	57.5	56.5	52.6
FIA (% paraffin)	69.7	67.5	52.1	46.4	37.7
FIA (% olefin)	0.4	0.6	17.2	16.6	17.6
FIA (% aromatic)	28.5	25.7	29.8	28.9	34.6

During the 1-hour period of temperature increase, a flame ionization detector (FID) continuously monitors the THC concentration inside the sealed housing for evaporative determination (SHED). At the beginning and conclusion of the test period, 10-liter portable Tedlar bag samples are collected for subsequent analysis.

The diurnal test is followed by the urban dynamometer driving schedule (UDDS), representing emissions during a typical urban driving period. The UDDS includes a series of driving modes of varying times and speeds typical of urban driving conditions (idling, accelerations, steady state, and deceleration). One run consists of two tests, a cold-start test after a minimum 12-hour soak, and a hot-start test after a 10-minute soak. The cold-start test includes transient and stabilized phases. Bag samples of the tailpipe exhaust are collected during three periods of the test: 1) the cold-start transient phase, 2) the cold-start stabilized phase, and 3) the hot-start phase. Emissions from the stabilized phase are weighted with the cold-start and hot-start phases to determine a gram per mile exhaust emission rates. Highway load simulations were achieved with a Clayton CTE 50-D direct-drive water brake dynamometer. After the urban driving period, the test vehicle is returned to the evaporative SHED for a hot-soak test, and sample bags are collected in the same manner as with the diurnal evaporative test.

The tailpipe exhaust samples were analyzed for THC, CO, CO_2, NO_x, and ethanol content; evaporative samples for THC and ethanol content. THC was determined with gas chromatography, CO and CO_2 with NDIR instruments, NO_x with a chemiluminescence analyzer, and ethanol with gas chromatography. The THC-FID instrument normally used to measure total hydrocarbon emissions does not respond to oxygenated hydrocarbons with the same sensitivity as pure hydrocarbons. For example, ethanol response is lower than ethane response. Thus, determination of hydrocarbon emission rates with a THC-FID when the emissions include ethanol requires knowledge of the ethanol content and response relative to the hydrocarbon calibration gas, e.g., propane. Total hydrocarbon determination with gas chromatography, however, is based on the summation of individual hydrocarbon species and thus, not complicated by uncertain response to ethanol. An in-depth description of the procedure for the analysis of ethanol in exhaust and evaporative emissions is provided in Appendix A.

RESULTS AND DISCUSSION

Exhaust and evaporative emissions data is reported for the Mustang and LTD II in Table IV. To determine the impact of ethanol on exhaust and evaporative emissions, the results reported in Table IV are given as ratios of emission rates of the gasohol blend relative to the respective base fuel. Specific gram per mile exhaust emission rates and gram evaporative

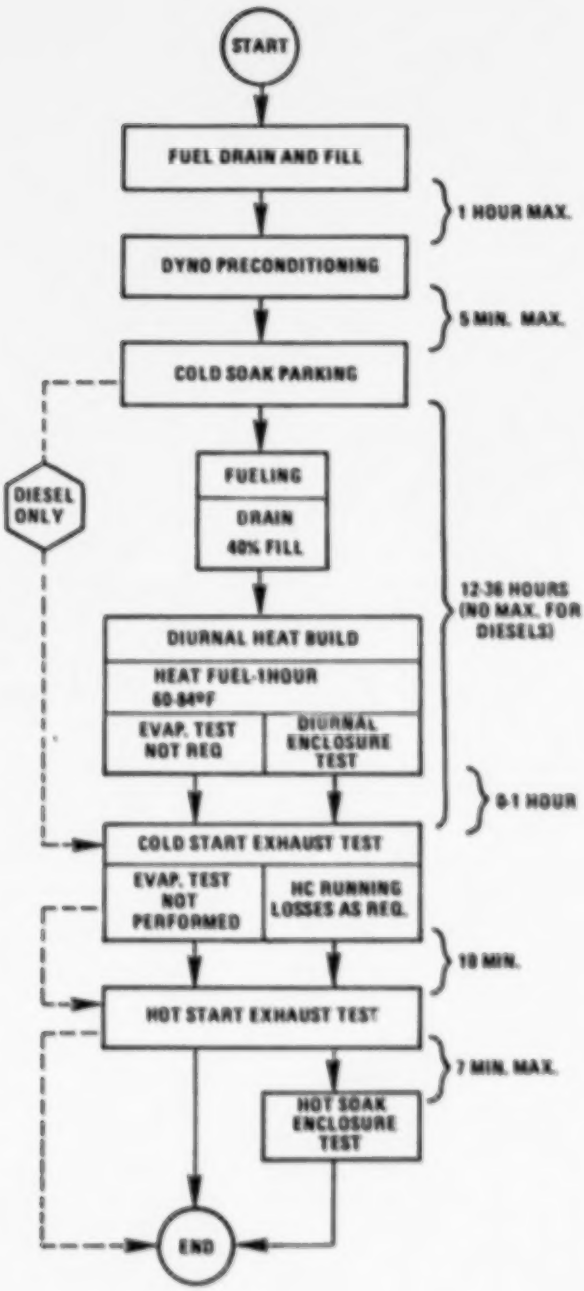

Fig. 2 - Vehicle test sequence

emission rates are reported for each test with each vehicle in Appendix B.

For the 1977 Mustang II, the addition of ethanol to the base fuel results in: 1) a decrease in THC emissions, 2) a decrease in CO emissions, 3) an increase in NO_x emissions, 4) undefined impact on fuel economy, and 5) a substantial increase in evaporative emissions.

Table IV - Ratio of emissions for 1977 Mustang II and 1979 LTD II[a].

Make	Fuel	THC[b]	CO	NO_x	Fuel Economy	Evap. THC[b]
Mustang	2/1	0.74	0.74	NA	0.95	2.53
LTD		0.74	0.72	1.35	1.01	3.15
Mustang	4/3	0.55	0.64	1.35	1.20	2.27
LTD		0.77	0.55	1.19	0.99	3.17
Mustang	5/3	0.84	0.94	1.17	0.90	1.53
LTD		0.92	0.76	1.14	1.04	2.71

[a] gasohol/base fuel
[b] sum of hydrocarbons and ethanol; g/mi for tailpipe, g/test for evaporative

A review of the influences of A/F ratio on exhaust emissions (Figure 1) indicates the basis of this trend. A lean shift in combustion is expected with gasohol because of the fuel's oxygen content. Since the Mustang II was operating with a base carburetor tune richer than the certification value as previously indicated, a condition typical of many passenger cars, a lean shift in combustion would logically increase the emissions of NO_x while decreasing THC and carbon monoxide emissions. The lean shift had no effect on driveability and an undefined effect on fuel economy. The lean shift probably displaced the A/F ratio closer to a more fuel economic tune, offsetting the loss in fuel economy resulting from the lower energy value of ethanol. The variability in fuel economy impact observed with the Mustang exceeds anything possibly resulting from the ethanol in the fuel. The malfunction condition of this vehicle resulted in test result variability requiring many more repetitions than program resources would support for accurate observations.

Results obtained with the LTD II are also compiled in Table IV. With this vehicle the tests revealed that the addition of ethanol to the base fuel produced: 1) a decrease in THC emissions, 2) a decrease in CO emissions, 3) an increase in NO_x emissions, 4) little change in fuel economy, and 5) a substantial increase in evaporative emissions. Again, the changes in tailpipe emissions can be explained by leaner combustion. The hydrocarbon situation was complicated, however, by a driveability problem: difficulty with cold-start operation. Table V reports the exhaust THC for each test phase of the UDDS. Test Phase 1 THC emissions increased substantially with use of gasohol in the LTD II. Driveability problems were apparent during cold-start operation with the engine stumbling and running roughly. A net increase of 0.82 grams THC was recorded for test phase one, while the remaining phases showed the net decreases predicted by leaner combustion. In contrast, a net decrease in THC occurred for each test phase

Table V - Exhaust HC per test phase (g/test phase).

Fuel	1977 Mustang II Phase 1	Phase 2	Phase 3
1 (Indolene)	14.5	16.6	10.4
2 (1 + Ethanol)	14.3	11.4	6.4
Net Difference	-0.2	-5.2	-4.0

Fuel	1979 LTD II Phase 1	Phase 2	Phase 3
1 (Indolene)	2.98	1.21	1.33
2 (1 + Ethanol)	1.80	0.87	0.66
Net Difference	-0.82	-0.34	-0.68

with the Mustang II, although the smallest decrease was observed in test phase 1.

Evaporative emission increases were significant with both vehicles. The 1977 Mustang II showed a net increase of 111% and the 1979 LTD II exhibited a net increase of 201%. Ford Motor Company has also reported data documenting substantial evaporative emissions increases with gasohol.(8) In their study, a fleet of nine vehicles averaged an evaporative emissions increase of 140%, ranging from 0 to 480%. The changes in fuel distillation characteristics and vapor pressure when ethanol is added contributes to differences in evaporative emissions. However, even with fuel 5, gasohol blended to match the distillation properties of base fuel 3, evaporative emissions increases were experienced with both test vehicles. This increase may be due to a relationship between the defined purge period for the canister and the chemical properties of ethanol. Possibly, because ethanol is a more polar organic than normal gasoline fuel components, it is more difficult to remove from the canister during purge. Effective capacity of the canister would thus decrease over a period of time. Furey and King have reported the same trend of higher evaporative emissions with the adjusted gasohol compared to gasohol.(9) Their study concluded that progressive deterioration of the rubber (nitrile) hose which vents fuel vapor from the carburetor float bowl to the canister resulted in higher emissions over a period of time.

In an effort to examine the sensitivity of the emissions to vehicle preconditioning, a short two test series was completed with the 1979 LTD II during which emissions with a single LA-4 cycle prep were compared with a RRR plus LA-4 prep. The LA-4 cycle consists of phases 1 and 2 of an FTP cycle. The RRR is the standard road course described previously in the text. Fuel 4 was selected for this comparison because it was the highest evaporative fuel tested. The results presented in Table VI suggest that the vehicle is operating slightly richer after a single LA-4 cycle prep, indicated by higher THC and CO emissions and lower NO_x emissions. The evaporative data shows substantially higher diurnal emissions with the LA-4 prep resulting from less complete regeneration of canister capacity during the single LA-4 prep sequence than during the combined RRR plus LA-4 prep sequence suggesting higher initial canister loads.

A final area of concern examined during the program was the adequacy of a one-hour soak to determine hot soak evaporative emissions. During the series of tests with the 1979 LTD II, the hot soak test was extended a second hour. Additional emissions were observed with each fuel, as reported in Table VII. The increase in hydrocarbon level during the second hour was reasonably constant at about 0.49 grams, thus the percentage increase was higher for the lower emission base fuels, averaging about 37 percent, than the high emission gasohol fuels, averaging about 10 percent.

The data indicates that a one hour soak may not be adequate for determining hot soak evaporative emissions. It appears that the levels of evaporative emissions from vehicles fueled with regular unleaded fuel may be underestimated, overestimating the magnitude of evaporative emissions increases with gasohol. This limited data suggests the need for a more comprehensive examination of the adequacy of certification procedures for determination of evaporative emissions factors.

With tailpipe hydrocarbon emissions decreasing and evaporative hydrocarbon emissions increasing, the aggregate must be examined to determine the actual impact of blending ethanol with gasoline. Figure 3 illustrates the relative abundances of tailpipe and evaporative hydrocarbon and ethanol emissions and the aggregate changes as a function of fuel. To permit direct comparison of evaporative emissions with tailpipe emissions, the evaporative emissions

Table VI - Emissions as a function of vehicle preparation[a]

Prep. Sequence	FTP, g/mi THC	CO	NO_x	Ethanol
RRR+LA-4	0.38	5.59	2.14	0.011
LA-4	0.52	8.12	2.01	0.012

Prep. Sequence	Evap., gm Diurnal HC	Hotsoak HC	Ethanol	Total
RRR+LA-4	1.26	5.13	0.81	7.20
LA-4	5.38	4.82	0.86	11.06

[a] fuel 4 only, average of two tests

Table VII - HC emissions during extended hot-soak.

Fuel	Evaporative, grams THC (1st hour)	THC (2nd hour)	$(THC_1+THC_2)/THC_1$
1	1.07	0.46	1.43
2	3.53	0.48	1.14
3	1.65	0.49	1.30
4	6.49	0.54	1.08
5	4.06	0.47	1.10

were reported in gram/mile equivalent rates using the relationship:(10)

$$Evap = \frac{Di + 3.3 \text{ trips/day } (Hs)}{29.4 \text{ miles/day}}$$

Evap = total evaporative emissions, grams/mile
Di = diurnal evaporative emissions, grams/day
Hs = Hot soak evaporative emissions, grams/trip

For the higher emission rate Mustang II, the aggregate had little sensitivity to fuel with tailpipe decreases being near equivalent to evaporative increases. The LTD-II aggregate, however, was sensitive to the fuel. The gasohol fuels resulted in hydrocarbon emissions 25 to 50 percent higher than with the gasoline base fuels.

CONCLUSIONS

The primary objective of this study was to examine the impact of gasohol on vehicle evaporative and tailpipe emissions. With both vehicles, the addition of ethanol to gasoline resulted in a decrease in THC and CO emissions and an increase in NO_x emissions. This was a result of a lean shift in combustion due to the oxygen content of ethanol. Both vehicles showed little change in fuel economy. The lower energy content of the ethanol fuel offset any improvements in fuel economy expected by leaner combustion. Driveability problems were experienced with the LTD II with the gasohol fuels. The use of gasohol in both cars substantially increased evaporative emissions. The change in aggregate, tailpipe plus evaporative, hydrocarbon emissions with gasohol varied from no significant change with the Mustang II to a maximum increase of about 50 percent with the LTD-II.

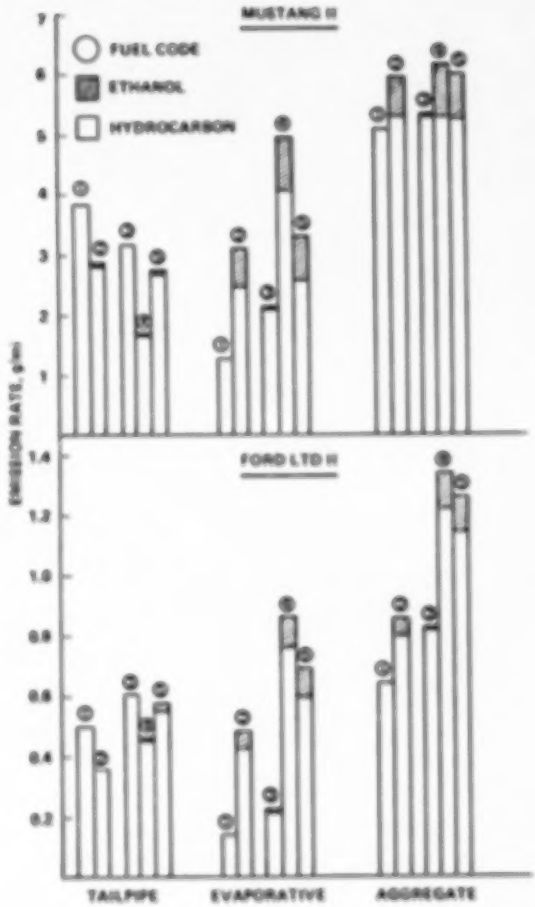

Fig. 3 - Effect of gasohol on emissions

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APPENDIX A

ANALYSIS OF ETHANOL IN EVAPORATIVE AND EXHAUST EMISSIONS FROM VEHICLES FUELED WITH GASOHOL

Exhaust emissions from motor vehicles are very complex mixtures of compounds including hydrocarbons, carbon numbers 1 to 10, aldehydes and ketones, carbon monoxide, nitric oxide, carbon dioxide and many others. The evaporative emissions are similarily complex, being dominated by the range of hydrocarbons in the fuel, carbon numbers 4 to about 10. Gasohol, a possible alternative to gasoline fuel, is a blend of alcohol with gasoline.

Examination of emissions from vehicles fueled with gasohol requires the use of analytical procedures permitting selective determination of ethanol in the presence of many other compounds. Gas chromatography is the obvious choice because of its capacity to resolve very complex mixtures. The chromatographic system described herewith permits quantitative determination of ethanol in samples obtained from vehicles fueled with gasohol.

Figure A-1 schematically illustrates the chromatographic inlet, column, and detection system. The analytical column is 10' X 1/8" stainless steel tubing packed with 15% 1,2,3, - tris (cyanoethoxy) propane on 60/80 mesh Chromosorb P. The column is maintained isothermal at 50°C. with a helium carrier flow rate of 30 cc/min. The 10 cc gas sample volume used permits accurate determination of 0.1 ppm C ethanol (standard deviation ± 10% of mean) with the

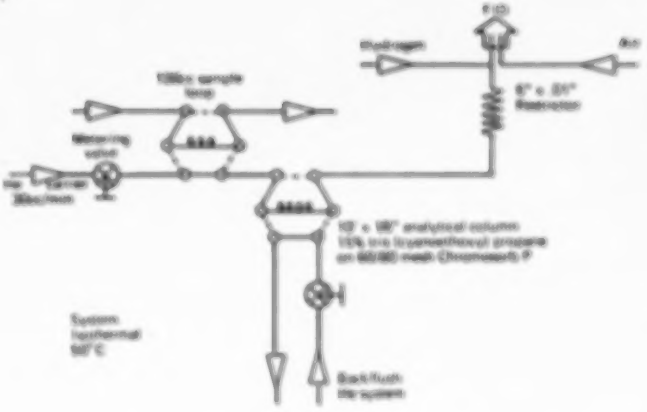

Fig. A-1 - Ethanol gas chromatographic system

flame ionization detector used (Perkin - Elmer 3920). This lower limit can be extended through use of larger sample volumes, but is adequate for the application under consideration.

Figure A-2 illustrates a typical chromatogram obtained with this system. Ethanol is baseline resolved, eluting between benzene and toluene. The "Tris" column elutes the paraffinic and olefinic compounds before the lowest molecular weight aromatic compound, benzene. Only the higher molecular weight aromatics elute after ethanol, e.g. toluene, p,m, and o-xylene. The ethanol peak elutes about 14 minutes after injection. Toluene, an abundant component of gasoline, is present in all vehicle samples, and for that reason serves as a good "fingerprint" compound to monitor the analytical system stability.

The system is configured to permit backflushing the analytical column of the high molecular weight residual compounds in preparation for successive analysis. However, if analysis of toluene is included, no significant reduction in analytical "turn-around time is obtained with this practice. The sample to sample time is about one hour with either backflushing or awaiting elution of the final aromatic peak of significance.

Calibration of the gas chromatograph is achieved using samples prepared by diluting known volumes of benzene, toluene, and ethanol (anhydrous) in air. These samples can be accurately prepared using the apparatus of Figure A-3. Known volumes of the liquids of interest are injected with a microliter syringe into the heated mixing zone (150° C) of the apparatus. The liquids are flash vaporized and swept into a Tedlar bag with a volume of air measured by a dry test meter. The concentrations of each compound are calculated (1 ul ethanol injected into a 10 l bag yields about 42 ppm molar or 84 ppm carbon depending on ambient temperature and

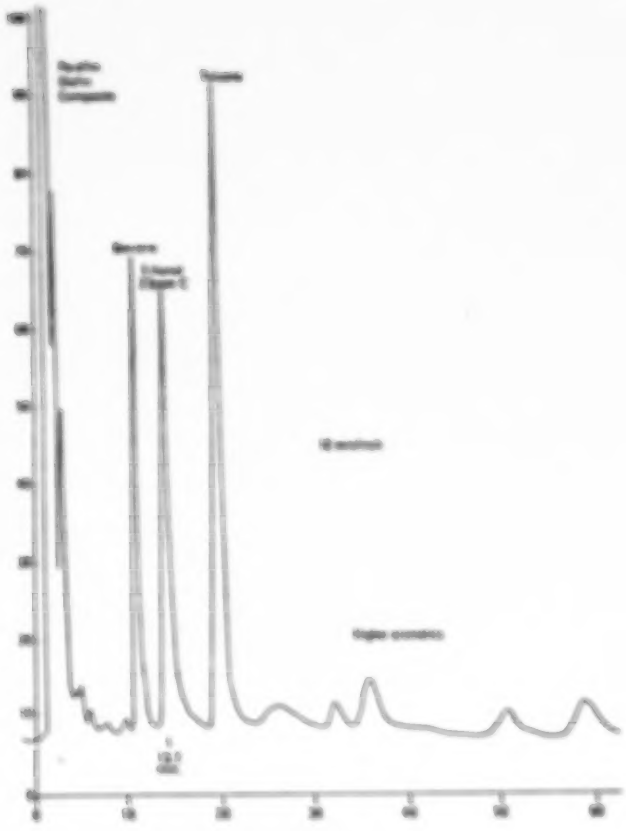

Fig. A-2 - Ethanol in auto exhaust

pressure) and the response of the FID to each determined on analysis with the gas chromatograph. The per unit carbon response of the FID is less for ethanol than the aromatics. With the Perkin - Elmer FID, the ethanol carbon response was determined to be 85 percent of the benzene carbon response. The benzene and toluene carbon response values were essentially identical.

A prime concern in the determination of ethanol emissions from the automobile is transport of the sample from the vehicle to the analyzer, i.e. sampling conditions. Sampling in Tedlar bags is desirable due to their common use for sampling THC, CO, and NO_x in the current certification practice. Bag wall losses constitute a prime concern, along with stability in the sample mixture. Several experiments were conducted to examine these potential problems.

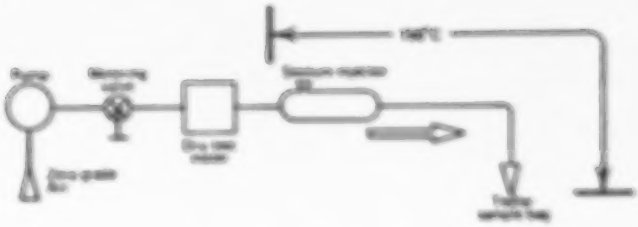

Figure A-3 - Apparatus for preparation of calibration mix

Ethanol samples were prepared in 10 liter bags with air, gasoline, and exhaust balances followed by analysis over defined time intervals. The results are given in Table A-I. The greatest loss observed was 8% on overnight storage. Care must be taken to assure that the exhaust sample water level does not exceed the dewpoint. Ethanol is very soluble in water and thus is readily lost if water droplets form on the walls of the bag. This situation can exist if the temperature and relative humidity of the CVS diluent air are high and the exhaust - air dilution ratios are low (large engines), particularly if the bag samples are carried into a cool air conditioned lab for chromatography.

With the bag stability considered adequate, a short series of experiments were conducted during which line losses were examined in the 1/4" stainless steel tubing used to transport the samples from the evaporative SHED to the tedlar bags. The sample lines were 25 feet long and at ambient temperature. The sampling rate was 0.25 liter/minute. There were no measurable losses of ethanol observed over the range, 15 to 100 ppm C, examined. Again it is very important to avoid condensed water vapor in the sample lines. This should not present a problem in evaporative testing, but potentially could in exhaust testing.

The procedures as described are adequate for determination of ethanol emissions from vehicles operated with gasohol fuel. The 1 hour analytical time potentially could be lessened by temperature programming the column to accelerate elutin of the higher aromatics. However, ethanol stability with storage in Tedlar bags is adequate to permit the one hour sample "turn - around" time. The exhaust and evaporative mass emission rates are calculated using the Federal Register equations for hydrocarbons, but substituting a density value of 27.1 g/cu. ft. for ethanol where necessary.

TABLE A-1. Ethanol storage stability
observed concentration ratio, original cnc./conc. at time x

Sample	0 hr	1 hr	2 hr	16 hr	24 hr
98 ppm C ethanol in air	1.00	1.02	1.02		
27 ppm C ethanol in air	1.00	1.05			
17.5 ppm C ethanol in air	1.00				0.97
69 ppm C ethanol in auto exhaust	1.00			0.94	
13.8 ppm C in gasoline	1.00			0.95	
10.5 ppm C in gasoline	1.00			0.93	
154 ppm C ethanol in gasoline	1.00			0.95	
23 ppm C ethanol in auto exhaust	1.00	1.01		0.92	

APPENDIX B

TABLE B-1. Exhaust emission rates for 1977 Mustang II

Fuel	gram/mile THC[a]	CO	NOx	Ethanol	Fuel economy
1	3.83	26.7	NA	0	15.5
2	2.82	19.8	1.53	0.026	14.7
3	3.15	27.0	1.27	0.002	14.3
4	1.72	17.2	1.72	0.024	17.1
5	2.66	25.5	1.48	0.044	12.8

[a] sum of hydrocarbons and ethanol

TABLE B-2. Evaporative emissions for 1977 Mustang II

Fuel	grams HCD	HCHS	Total	Ethanol	HC+Ethanol
1	0.42	10.60	11.02	0.05	11.07
2	0.32	22.10	22.40	5.59	27.99
3	0.42	18.80	19.22	0.29	19.51
4	0.34	36.10	36.44	7.80	44.24
5	0.51	22.90	23.41	6.51	29.92

TABLE B-3 - Exhaust emission rates for 1979 LTD II

Fuel	gram/mile THC[a]	CO	NO_x	Ethanol	Fuel economy
1	0.50	12.7	1.36	0	11.3
2	0.37	9.2	1.83	0.002	11.4
3	0.60	10.3	1.85	0	11.0
4	0.46	5.7	2.20	0.012	10.9
5	0.55	7.8	2.10	0.023	11.4

[a] sum of hydrocarbons and ethanol

TABLE B-4 - Evaporative emissions for 1979 LTD II

Fuel	grams HCD	HCHS	Total	Ethanol	HC+Ethanol
1	0.47	1.07	1.54	0.03	1.57
2	0.86	3.53	4.39	0.55	4.94
3	0.86	1.65	2.51	0.07	2.58
4	0.74	6.49	7.23	0.94	8.17
5	1.22	4.86	6.08	0.91	6.99